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A FULLY-INTEGRATED MEMS PRECONCENTRATOR FOR RAPID GAS SAMPLING (PREPRINT)

Byunghoon Bae, Junghoon Yeom, Adarsh D. Radadia, Richard I. Masel, and Mark A. Shannon

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14. ABSTRACT
A new type of fully integrated MEMS preconcentrator has been fabricated and tested as a front end for a flame ionization detector (FID). A 1 microliter preconcentrator filled with PEI-coated microposts is integrated with fast microvalves (response time < 50 μs) and a resistive microheater (ramping to 200 ºC in 0.5 second). The integrated preconcentrator can sample a cubic centimeter of gas in 0.2 second at 50 kPa, adsorb targeted species, heat and desorb in 0.5 second, and inject concentrated gaseous species in as small as 50 μs pulses into separation columns in a microscale gas chromatograph (GC), or directly into a detector. The unprecedented speed of this preconcentrator (< 1 second) is enabled by MEMS sizing and fabrication, allowing sniffing of chemical warfare agents, toxic industrial compounds (TICs), and other volatile compounds in seconds, rather than tens of minutes with conventional systems.

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preconcentrator, MEMS, microposts, microvalves, toxic gases

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A FULLY-INTEGRATED MEMS PRECONCENTRATOR FOR RAPID GAS SAMPLING

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ABSTRACT
In this paper, we present a new type of MEMS gaseous species preconcentrator (μPC) that has been fabricated and tested as a front end for a flame ionization detector (FID). A one microliter μPC filled with microposts is integrated with microvalves (response time < 50 μs) and a resistive microheater (ramping to 200ºC in 0.5 seconds). The integrated μPC can sample a cubic centimeter of gas in 0.2 seconds at 49 kPa, adsorb targeted species, heat and desorb, and inject concentrated gaseous species with 25 microsecond pulses into separation columns and/or detectors. The unprecedented speed of this μPC is enabled by MEMS sizing and fabrication, allowing sniffing of phosphonates, toxic industrial chemicals (TICs), and other volatile compounds in seconds, rather than tens of minutes with conventional systems.

Keywords: Preconcentrator, Microvalve, Microheater

I. INTRODUCTION

Many efforts are being made to develop a microfabricated GC system (μGC) that is small enough to be carried by individuals [1,2]. A micro pre-concentrator (μPC) is a key component in such a device. The μPC increases the concentration of analytes from low concentration (e.g. part-per-billion) to higher concentrations (e.g. parts per million) so low concentrations of analytes can be easily detected [1]. Micro-PCs, including a heated membrane with a thin adsorbent layer, were developed by Frye-Mason *et al*. for detecting specific chemical warfare agents [3]. Tian *et al*. developed a multiple-stage microfabricated PC with a large adsorbent capacity [4,5].

In this paper, we present for the first time a new type of fully integrated MEMS μPC that has been fabricated and tested for the rapid concentration of vapor species that are introduced to a flame ionization detector (FID). A one microliter μPC filled with polyethyleneimine (PEI) coated microposts is integrated with fast microvalves [6] (response time < 50 μs) and a resistive microheater (ramping to 200ºC in 0.5 seconds) [7]. The integrated PC can sample a cubic centimeter of gas in 0.2 seconds with a 50 kPa inlet pressure, adsorb targeted species, heat and desorb them in 0.5 s, and inject the now concentrated gaseous species using fast acting microvalves in pulses as small as 50 microsecond into separation columns in a μGC, or directly into a detector. The unprecedented speed of this μPC (< 1 s) is enabled by MEMS sizing and fabrication, allowing sniffing of phosphonates, toxic industrial compounds (TICs), and other volatile compounds in seconds, rather than tens of minutes with conventional systems. The micropost structures, which are subsequently coated with PEI, are fabricated using deep reactive ion etching to achieve a high surface area-to-volume ratio while

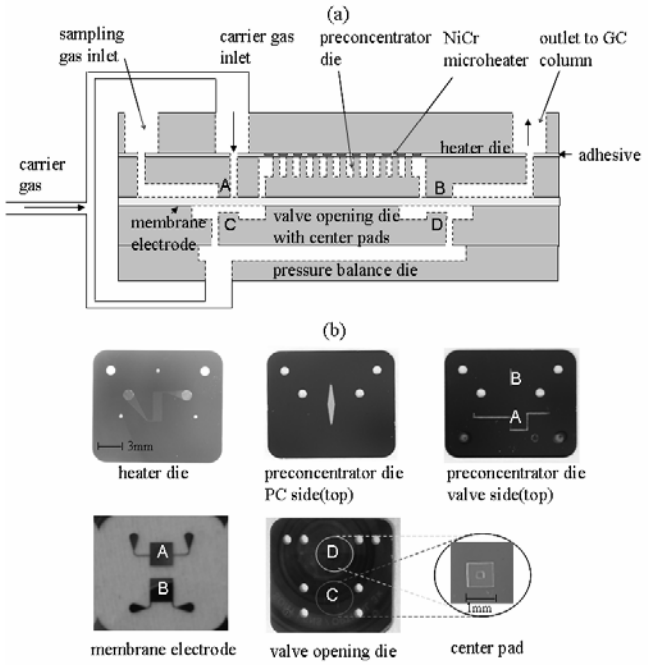

Figure 1: (a) A schematic cross-sectional diagram of the integrated preconcentrator consisting of a NiCr microheater, a 1 μl preconcentrator, and two microvalves. (b) Device pictures of the layers corresponding to (a).

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permitting a relatively low pressure drop during the loading and injecting phases of operation in order to reduce both power consumption and analysis time [8].

II. DESIGN

Figure 1 shows a schematic diagram and device pictures of the integrated μPC. It consists of a NiCr microheater, the posted preconcentrator cavity, and two electrostatic microvalves. The NiCr microheater heats the silicon surface immediately adjacent to the μPC to subsequently heat the gas and analyte up to 200°C using a feedback control of resistance-temperature relationships obtained in off-line calibration.

The microvalves are composed of a valve seating electrode, whose topside the μPC is integrated within, a membrane electrode, and a valve opening electrode. The membrane is fabricated with two patterned metal (Cr/Au/Cr: 50Å/500Å/50Å) electrodes embedded in polyimide (two layers, 3 μm thick). The membrane electrodes located at the inlet (A) and outlet (B) of the μPC, respectively, are opened by applying a voltage V_1 and closed by applying V_2, as shown in Fig. 2. This feature enables the injection band width from the μPC to be controlled by the operation of the microvalves, rather than by a slower desorption heating rate.

Figure 2 illustrates the (a) on and (b) off operation of the microvalves, as well as important features contributing to a switching performance on the order of microseconds. These features include pneumatically balanced membranes (by P_1), which is designed to have almost zero net-pressure across the membrane to handle increasing pressures, and center pads which are designed to increase the electrostatic force between the membrane and the lower electrode. Figure 3 shows scanning electron microscope (SEM) images of the cross-sectional view of the integrated μPC, with close-ups of the Si-microposts and one of the microvalves.

III. FABRICATION

Figure 4 illustrates the fabrication process of the preconcentrator die. (a) It starts with an (100) silicon wafer. (b) Photoresist (PR) is patterned for the channels and holes on the valve side. (c) PR is

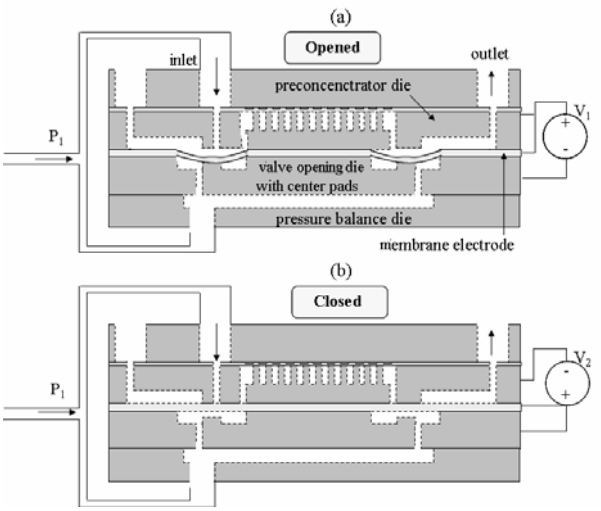

Figure 2: (a) A schematic diagram of the PC when the valves are opened, and (b) closed.

patterned for the microposts on the preconcentrator side using double side alignment with the valve side. (d) After a hardbake, deep reactive ion etching (DRIE) creates the channels, holes, and microposts. The valve side is then doped with boron in a diffusion furnace tube to make the Si-pattern conductive, following by growing a dielectric thermal oxide layer over the conductive layer to prevent later electrical shorting. (e) To create ohmic contacts in the doped Si layer, PR patterns define openings where the thermal oxide is removed, and a Cr/Au (50Å/1000Å) stack is sputtered on and the excess lifted-off with the removal of the PR. (f) Finally, non-stiction $[CF_2]_n$ layers are deposited using a C_4F_8 plasma where the membranes will touch the Si electrodes using a shadow mask for patterning. The fabrication process of the valve opening die is

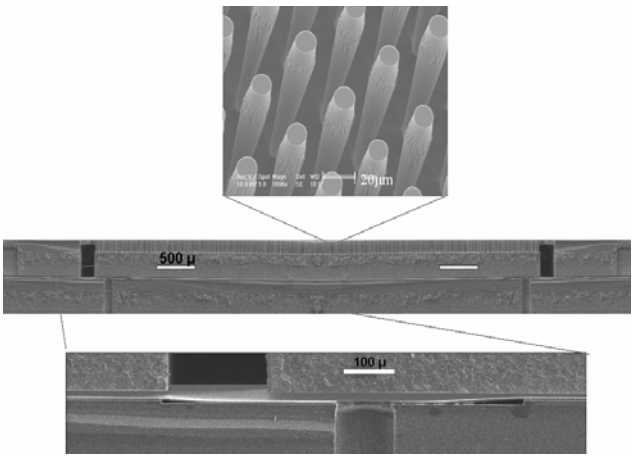

Figure 3: SEM images of the cross-sectional view of the integrated PC (center), microposts in the PC (top), and a cross-sectional view of the microvalve (bottom).

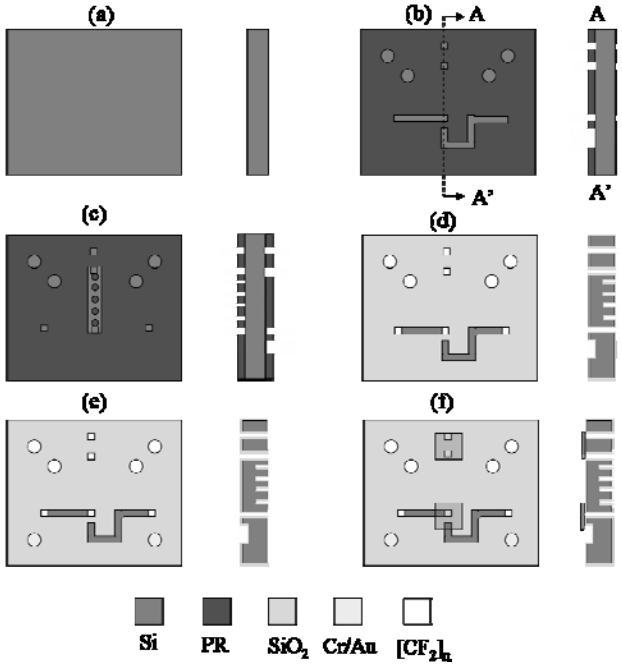

Figure 4: Fabrication process of the preconcentrator die for the integrated preconcentrator.

the similar to the valve closing die. Refer to [6] for the fabrication process of the membrane.

Figure 5 illustrates the fabrication process of the microheater. (a) It starts with an (100) silicon wafer. (b) The holes for fluidics are patterned, and etched using DRIE. Then, a dielectric thermal oxide layer is grown over the silicon for insulation of the heater. (c) NiCr is sputtered and patterned to make a serpentine by PR patterning and successive wet etching. (d) Au pads are made by the same method as the NiCr serpentine.

IV. RESULTS

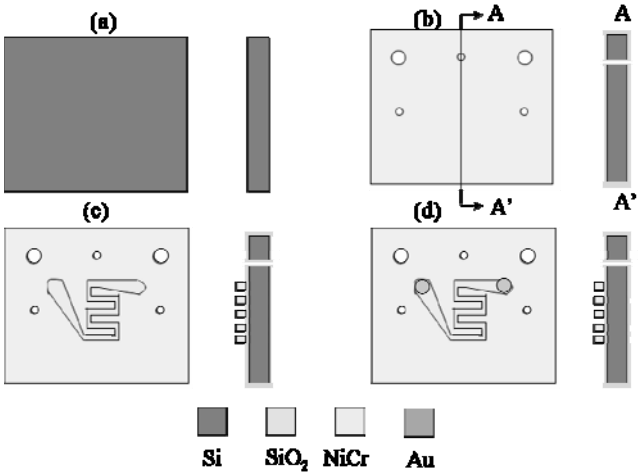

Figure 5: Fabrication process of the heater die for the integrated preconcentrator.

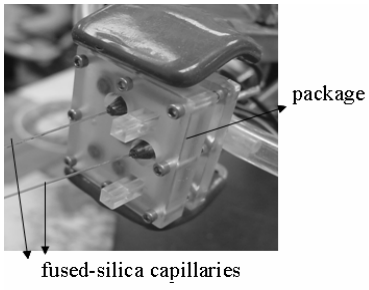

Figure 6: Enclosed sample using a package with fused-silica capillaries attached coming from the gas feed and exiting to the FID.

Figure 6 shows a packaged integrated µPC with fused-silica capillaries attached. An FID is used to check the output of the µPC. Dimethylmethanephosphonate (DMMP) is vaporized in a bubbler and 1 ppm is injected with nitrogen carrier gas from the µPC to the FID.

Figure 7 shows the closing time ranging from 30 to 50 µs of the microvalve at different pressures from 42 to 126 kPa.

Figure 8 shows the FID output with and without the µPC coated with PEI. In (a) the FID signal is shown for a 100 µs microvalve pulsewidth to the column to demonstrate short band injections. In (b) the FID signal is shown for DMMP adsorbed in the µPC, desorbed while heating to 200ºC, and then opening the valve. The ratio of the mass of DMMP detected by the FID with and without the µPC shows a gain of ~ 320 for this PEI coated integrated µPC over that of directly detecting the species without the µPC.

V. CONCLUSIONS

We developed an integrated microposted

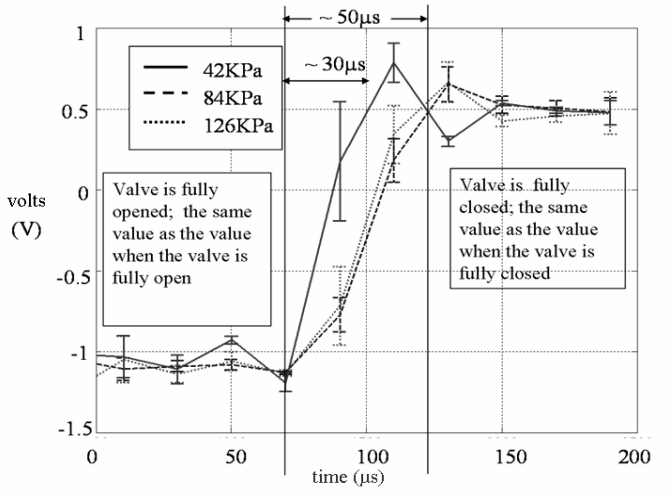

Figure 7: Switching performance of the microvalve showing closing of the valve in 30 to 50 microseconds for 3 different gas pressures.

preconcentrator that consists of a microsecond switching microvalve, and a resistive microheater. Testing the integrated μPC, a sharp band can be generated, as well as high gain in the FID signal, which enables higher resolution detection schemes. Therefore, this integrated μPC can contribute to a more sensitive and faster response for μGC, such that chemical species below ppm can potentially be detected within seconds.

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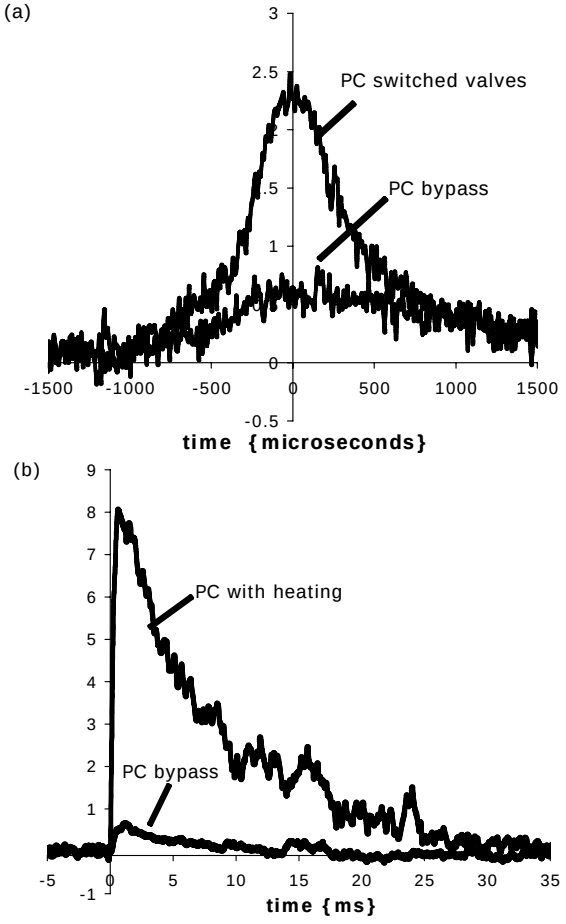

Figure 8: (a) FID signal of DMMP in N_2 with and without going through the μPC with posts coated with PEI. Microvalve switching with a 100 μs pulsewidth gives downstream 1/e width of ~1000 μs at FID. (b) FID signal of DMMP in N_2 with and without going through same μPC undergoing heating to desorb DMMP. Valve opened after heating and detecting all mass leaving the μPC with FID gives